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Technique for recovering rare-earth metals from spent sintered Nd-Fe-B magnets without external heating

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ABSTRACT

To selectively recover rare-earth metals with higher purity from spent sintered Nd-Fe-B magnets without external heating, we investigated the mechano-chemical treatment of spent sintered Nd-Fe-B magnet powder with a reaction solution of HCl and $(COOH)_2$ at room temperature. The results of various experiments showed that the mechano-chemical treatment with HCl and $(COOH)_2$ is very effective for recovering the rare-earth metals contained in spent sintered Nd-Fe-B magnet powder; the recovery rate and purity of the rare-earth metals were 95.3 and 95.0 mass%, respectively, under optimal conditions ($[HCl] = 0.2\ mol/dm^3$ and $[(COOH)_2] = 0.25\ mol/dm^3$).

1. Introduction

Sintered Nd-Fe-B magnets, originally researched and developed by Sagawa et al. [1–3], have the strongest coercive force among currently available magnets. Nowadays, sintered Nd-Fe-F magnets are employed as one of the essential components of the micro-motor of hard-disk drives and DVD recorders. In addition, they are used in compact speakers, watches, smartphones, automobiles, hybrid vehicles, and electrical appliances. The future demand for Nd-Fe-B magnets is expected to grow rapidly, especially because of the need for miniaturized and high-performance manufactured goods. In view of this expectation, the securement of rare-earth ores, which are essential for manufacturing Nd-Fe-B magnets, has been proposed as a high-priority national policy. However, it is extremely difficult for Japan to secure such ores because of its extremely low self-sufficiency rate. Therefore, the Japanese government and industries are devoting considerable effort toward the development of novel and independent industrial processes for stably securing rare-earth ores, which will be relatively unaffected not only by the international economic situation, but also by the diplomatic relations between Japan and rare-earth metal producing countries or the domestic situation in such countries. Toward this end, there is an urgent requirement for an effective industrial system for recovering rare-earth metals from solid waste, such as spent sintered Nd-Fe-B magnets, as industrial raw materials for obtaining rare-earth metals of higher purity.

To expedite the establishment of such high-efficiency industrial processes, techniques for recovering rare-earth metals from various types of solid waste containing such elements have been investigated by many researchers from different fields such as metallurgy, applied chemistry, and chemical engineering. Machida et al. [4] reported that Nd could be recovered as $NdCl_3$ in around 90% yield by calcination of Nd-Fe-B magnet scrap and NH_4Cl at 573 K for 3 h. Moreover, they showed the possibility of obtaining residues containing Fe as an electro-microwave absorbent. Okabe et al. [5,6] reported that pure Nd metal (97.7% purity) could be recovered by treating Nd-Fe-B magnet scrap at temperatures above 1000 K. In this process, Nd metal can be directly collected using Mg alloy as the extraction medium. However, this process suffers from high energy costs and low product purity. Mochizuki et al. [7] reported that the rare-earth metals contained in oxidized Nd-Fe-B magnet scrap could be selectively recovered by chlorination under a Cl_2 gas stream at temperatures up to 1273 K. However, this process has a high energy cost; in particular, the maintenance cost is extremely high owing to the corrosive nature of Cl_2 gas. Liao et al. [8] reported that Nd from Nd-Fe-B magnet scrap could be selectively leached by H_2SO_4 based on the results of leaching experiments using four leaching reagents: NaOH, HCl, HNO_3, and H_2SO_4. The recovery rate of Nd was 75.41 mass%, which was not sufficiently high. Shibayama et al. [9] reported higher recover rates of Nd and Dy (up to 98% and 81%, respectively) via a hydrometallurgical process using a mixed solution of HNO_3 and H_2O_2. Nd and Dy dissolved in the acid

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solution could be collected in oxalate form. Although these recovery rates are higher than those of reported dry processes such as chlorination and metallurgical process, they remain insufficient. To address the various problems faced by current and reported techniques for recovering rare-earth metals, the authors had previously reported a hydrothermal technique for recovering rare-earth metals from spent Nd-Fe-B magnets [10]. Thus, rare-earth oxalate salt with very high purity (≥99 mol%) could be selectively recovered from spent sintered Nd-Fe-B magnets without degaussing via hydrothermal treatment in a mixed aqueous solution of HCl and $(COOH)_2$ at 383 K for 6 h. The proposed hydrothermal technique makes it possible to recover rare-earth metals from spent Nd-Fe-B magnets as oxalate salts at a lower temperature and with a shorter treatment time than other techniques. However, this approach involves external heat treatment. Thus, it is not sufficient yet eco-friendly.

The authors have previously reported that mechano-chemical treatment with reaction solvents is an eco-friendly technique for recovering valuable metal resources from solid waste without external heating. For example, when spent Pb-glass powder is subjected to mechano-chemical treatment with ethylenediaminetetraacetic acid (EDTA) aqueous solution, Pb and Ba can be extracted as EDTA complexes [11]. Similarly, lead sulfate crystals can be effectively collected in solid form from lead zirconate titanate [12–14] and lead lanthanum zirconate titanate [15] sintered compacts via mechano-chemical treatment with sulfuric acid. In the present study, we investigated the recovery of rare-earth metals such as Nd and Dy from spent sintered Nd-Fe-B magnets via mechano-chemical treatment with a mixed aqueous solution of HCl and $(COOH)_2$ without external heating.

2. Experiment

2.1. Pretreatment of spent sintered Nd-Fe-B magnets

Spent sintered Nd-Fe-B magnets (chemical composition summarized in Table 1), which were acquired from a recycling company (ARBIZ Corporation) in Japan, were degaussed by heating at 573 K for 1 h in an electric furnace (SSFT-1520, Yamada Denki Co., Ltd.). The degaussed magnets were crushed into coarse grains using the planetary milling method at 300 rpm for 24 h with zirconia balls (diameter, 10 mm) and grinding bowl fasteners (P-5/2, Fritsch Japan Co., Ltd.). The degaussed and crushed magnet (hereafter, D&C/Nd-mag) powder was used as the sample powder for mechano-chemical treatment.

2.2. Mechano-chemical treatment of D&C/Nd-mag powder

Next, 0.5 g of D&C/Nd-mag powder was sealed in a polypropylene bottle (100 cm^3) with around 130 g of zirconia balls (diameter, 5 mm) and 20 cm^3 of HCl–$(COOH)_2$ mixed aqueous solution with appropriate concentration. For determining the optimal mechano-chemical conditions, the molar concentrations of HCl and $(COOH)_2$ were set in the range of 0.0125–0.2 mol/dm^3 and 0.005–0.85 mol/dm^3, respectively. Mechano-chemical treatment of D&C/Nd-mag powder was performed using a rotary ball-milling apparatus (UB-32, YAMATO Scientific Co., Ltd.) at 120 rpm for 6–24 h. After the mechano-chemical treatment, the produced precipitates adhered on the zirconia balls were collected by sonication for 3 min in 300 cm^3 of 0.02 mol/dm^3 HCl. The produced precipitates were completely collected by filtration under reduced pressure, and then, the collected precipitate was dried at 333 K overnight.

Table 1
Chemical composition of spent sintered Nd-Fe-B magnets.

	Nd	Dy	Fe	B	Ni[a]	Cu[a]
Content (mg/g)	152.9	42.4	332.8	1.4	12.3	1.2

[a] From plating.

2.3. Characterization

Quantitative analysis of the metals (Nd, Dy, Fe, Ni, Cu, and B) in the filtrate and acid aqueous solution obtained by fully dissolving the collected powder into HCl after mechano-chemical treatment was carried out via inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 2000DV, PerkinElmer Co., Ltd.). From this elemental analysis, both the recovery rate of each metal (R) and the purity of the rare-earth metals (P) were calculated as follows:

$$R(\text{mass\%}) = \frac{(m^{\text{solid},M})}{(m^{\text{solid},M}) + (m^{\text{liquid},M})} \times 100 \quad (1)$$

$$P(\text{mass\%}) = \frac{(m^{\text{rare-earth}})}{(m^{\text{total}})} \times 100 \quad (2)$$

where $m^{\text{solid},M}$ and $m^{\text{liquid},M}$ are the weight of each metal, M, in the collected solid and liquid, respectively, and $m^{\text{rare-earth}}$ and m^{total} are the weight of the rare-earth metals and all the metals in the collected solid, respectively. Here, the experimental errors of both R and P values were about 1% of each value. The precipitates collected after mechano-chemical treatment were identified via X-ray diffraction (XRD) analysis (MiniFlex-II, RIGAKU Corporation) using Mo-filtered Fe$K\alpha$ radiation (30 kV and 15 mA). The precipitate collected by mechano-chemical treatment under optimal condition was measured by thermal gravimetry-differential thermal analysis (TG-DTA: ThermoPlus II, RIGAKU Corporation).

3. Results and discussion

3.1. Effect of HCl concentration

The R value of each metal is plotted against the HCl concentration in Fig. 1, when the D&C/Nd-mag powder was treated via the mechano-chemical method with HCl–$(COOH)_2$ mixed reaction solution. Here, the concentration of $(COOH)_2$ was constant (0.1 mol/dm^3). The R values of the rare-earth metals did not change with increase in HCl concentration; they were nearly constant (around 60 mass%). Furthermore, the R values of Fe, B, and Ni did not

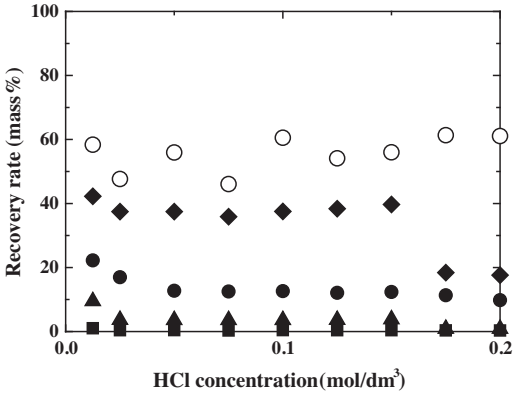

Fig. 1. Dependence of the R value of each metal on HCl concentration; $[(COOH)_2] = 0.1$ mol/dm^3. The symbols represent the following: rare-earth (○), Fe (■), B (●), Ni (▲), and Cu (♦).

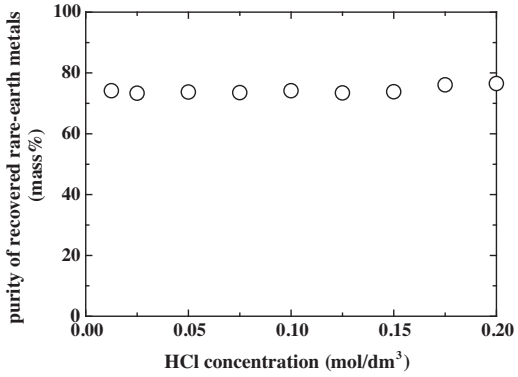

Fig. 2. Dependence of the *P* value of rare-earth metals on HCl concentration; $[(COOH)_2] = 0.1\ mol/dm^3$.

change with increase in HCl concentration; they were extremely low for Fe, 10 mass% for B, and around 5 mass% for Ni. The *R* value of Cu was around 40 mass% below 0.150 mol/dm^3 of HCl. However, it decreased to 20 mass% above 0.175 mol/dm^3 of HCl. Thus, it was assumed that the *R* value became the highest above 0.175 mol/dm^3 of HCl. The dependence of the *P* value on HCl concentration is shown in Fig. 2. The *P* values did not depend on HCl concentration, as in the case of the *R* values. XRD analysis showed that the precipitate collected by the proposed mechano-chemical treatment was a rare-earth oxalate salt, i.e., $Nd_2(C_2O_4)_3$, which could be used as an industrial ore (see Fig. 3). However, the *R* and *P* values were low (60 mass% and 80 mass%, respectively). These results indicate that the optimization of $(COOH)_2$ concentration would be required for improving the *R* and *P* values.

3.2. Effect of $(COOH)_2$ concentration

The dependence of the *R* value of each metal on the $(COOH)_2$ concentration is shown in Fig. 4. Here, the HCl concentration was constant (0.2 mol/dm^3). The *R* value of the rare-earth metals rapidly increased above 0.05 mol/dm^3 of $(COOH)_2$ and became saturated at 0.3 mol/dm^3 of $(COOH)_2$. The saturated *R* value was around 100 mass%. The *R* values of Fe, Ni, and Cu were nearly zero below 0.25 mol/dm^3 of $(COOH)_2$, and they increased with the $(COOH)_2$ concentration. Furthermore, the *R* value of B was nearly constant (30 mass%), even when the $(COOH)_2$ concentration was varied. This trend was due to the formation of soluble ionic species under various pH conditions. These results indicate that rare-earth metals contained in D&CNd-mag powder could be completely recovered by optimizing the $(COOH)_2$ concentration.

The dependence of the *P* value on $(COOH)_2$ concentration is shown in Fig. 5. The *P* value was extremely low below 0.05 mol/dm^3

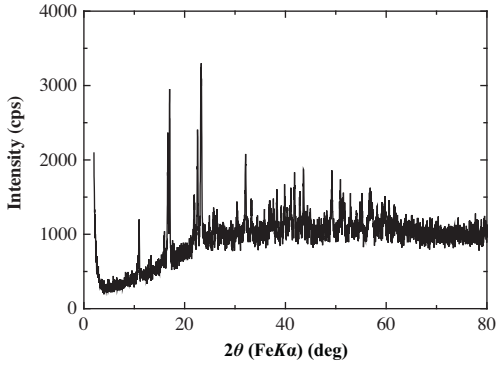

Fig. 3. XRD pattern of precipitate collected by mechano-chemical treatment.

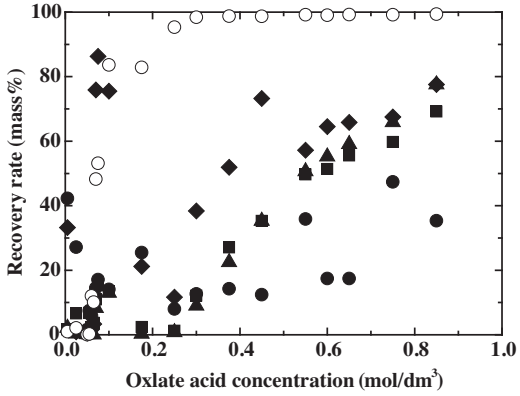

Fig. 4. Dependence of the *R* value of each metal on $(COOH)_2$ concentration; $[HCl] = 0.2\ mol/dm^3$. The symbols represent the following: rare-earth (○), Fe (■), B (●), Ni (▲), and Cu (♦).

of $(COOH)_2$ and rapidly increased in the range of 0.05–0.2 mol/dm^3 of $(COOH)_2$. When the $(COOH)_2$ concentration was increased above 0.25 mol/dm^3, the *P* value gradually decreased with increase in $(COOH)_2$ concentration. This decrease was synchronized with the increase in the *R* values of Fe, Ni, and Cu (see Fig. 4), i.e., this decrease was due to the production and precipitation of the oxalate salts of Fe, Ni, and Cu, as indicated by the XRD patterns of the recovered precipitate. From these results, it was concluded that the production of rare-earth oxalate precipitate had greater priority over the production of oxalate precipitates of the other transition metals (Fe, Ni, and Cu) under wet mechano-chemical treatment. Therefore, we could confirm that wet mechano-chemical treatment of D&C/Nd-mag powder with mixed reaction aqueous solution of HCl and $(COOH)_2$ is a highly effective method for selectively recovering rare-earth metals as oxalates from the D&C/Nd-mag powder without external heating. Moreover, the optimal concentrations of the reaction aqueous solution of 0.5 g of D&C/Nd-mag powder were $\geq$0.2 mol/dm^3 of HCl and $\geq$0.25 mol/dm^3 of $(COOH)_2$. Accordingly, the *R* and *P* values of the rare-earth metals in the precipitate recovered by the proposed mechano-chemical treatment under the optimal conditions were 95.3 and 95.0 mass%, respectively. Therefore, it can be concluded that mechano-chemical treatment is a novel and highly effective technique for recovering rare-earth metals from D&C/Nd-mag powder.

3.3. Effect of treatment time

The treatment time dependence of the *P* value in the case of the mechano-chemical and still-standing treatments is shown in Fig. 6.

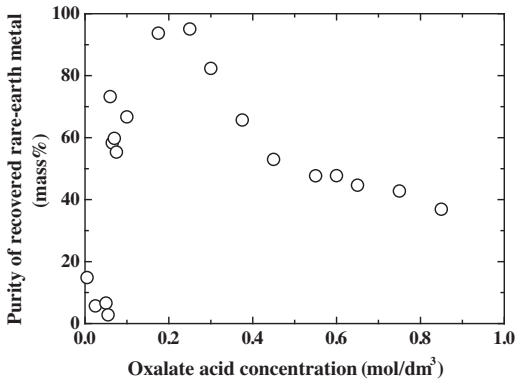

Fig. 5. Dependence of the *P* value of rare-earth metals on $(COOH)_2$ concentration; $[HCl] = 0.2\ mol/dm^3$.

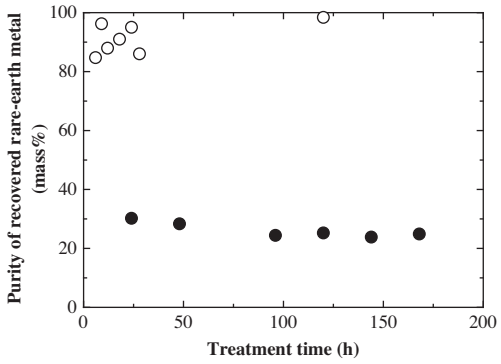

Fig. 6. Treatment time dependence of the *P* value of rare-earth metals; [HCl] = 0.2 mol/dm^3, [$(COOH)_2$] = 0.25 mol/dm^3. The symbols represent the following: mechano-chemical treatment (○) and still-standing treatment (●).

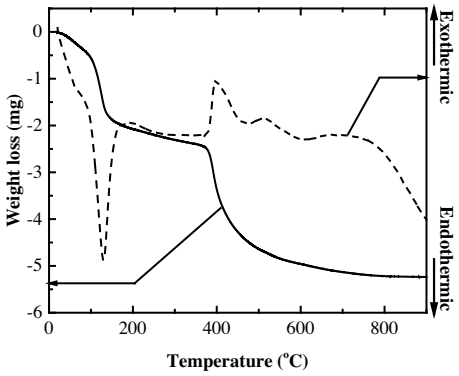

Fig. 7. TG-DTA curves of recovered rare-earth oxalate salt under optimal conditions.

The *P* value of the still-standing treatment is much lower than that of the mechano-chemical treatment. This indicates that mechano-chemical treatment with HCl—$(COOH)_2$ aqueous solution is a highly effective method for recovering rare-earth metal precipitate with high *R* and *P* values from D&C/Nd-mag powder.

3.4. Heat treatment of recovered oxalate salts

In Fig. 7, TG-DTA curves of rare-earth oxalate salt recovered by the mechano-chemical treatment of D&C/Nd-mag powder under optimal conditions are shown. In these curves, weight loss with endothermic change the temperature range from 100 to 150 °C and weight loss with exothermic change above 400 °C could be observed. It is well known that these changes are anhydration of crystallization water in rare-earth oxalate salt such as $Nd_2(C_2O_4)_3{\cdot}xH_2O$ and oxidation of $Nd_2(C_2O_4)_3$ with CO_2 generation, respectively. Here, it could be confirmed that solid powder after TG-DTA measurement was Nd_2O_3 from XRD analysis (cf. Fig. 8). Therefore, the rare-earth oxalate salt could be converted to Nd_2O_3 crystal, which is can be reused as starting materials for various industrial process.

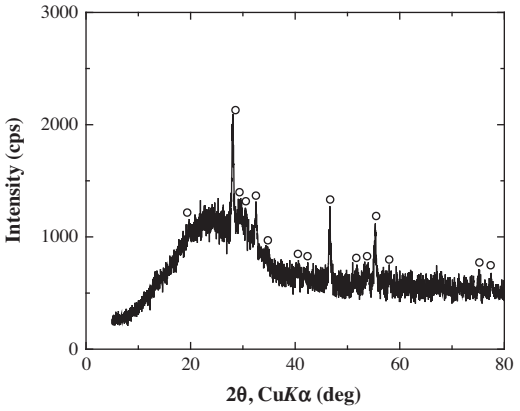

Fig. 8. XRD pattern of powdery sample obtained by heating the recovered rare-earth oxalate salt at 800 °C. Circles indicate diffraction peaks from Nd^2O^3.

4. Conclusions

To the best of our knowledge, this study is the first instance in which mechano-chemical treatment with HCl—$(COOH)_2$ mixed aqueous solution is shown to be a highly effective method for selectively recovering rare-earth metals as oxalate salts from spent sintered Nd-Fe-B magnets without external heating. Further, we found that the optimal concentrations of HCl and $(COOH)_2$ were 0.2 and 0.25 mol/dm^3, respectively. The recovery rate and purity of the rare-earth metals were 95.3 and 95.0 mass%, respectively.

Acknowledgements

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